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(54) **Poly(meth)acrylate ester based hydrogel adhesives**

Poly(meth)acrylate-Hydrogelklebmittel

Hydrogel adhésifs à base d'ester de poly(méth)acrylates

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• **J. DENT.**, vol.16, 1988, LONDON pages 76 - 79
POKORNY, DNEBOSKY 'the effect of acrylic acid
dimer on the properties of carboxycement'

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EP 0 676 457 B1

Description**FIELD OF THE INVENTION**

5 This invention relates to hydrogel adhesives and, more particularly, to polyacrylate and polymethacrylate ester based hydrogel adhesives used with biomedical devices.

BACKGROUND OF THE INVENTION

10 In the medical field, when a biomedical electrode is used on a patient, it is generally provided with a metallic plate attached to conductive wires which are, in turn, attached to a monitoring apparatus. To improve conductivity between the skin and the electrode, a composition, usually a paste, a gel, or a cream, is applied between the metallic plate and the skin. The use of such a composition is often messy and offensive to the patient. In addition, the composition must be removed from the skin after use, either by wiping or by the use of solvents, both of which are also offensive. Fur-
 15 thermore, the electrode is usually secured to the patient by tape having a conventional pressure sensitive adhesive (PSA) thereon. Removal of the tape causes discomfort to the patient, and the composition of the adhesive of the tape may induce an allergic reaction in the patient.

To circumvent these difficulties, electrically conductive hydrogel adhesives have been developed. These hydrogel adhesives have replaced pastes, gels, and creams because they advantageously provide both conductivity and clean,
 20 residue-free removal from the skin surface after use. In addition, depending on the particular application and electrode design and on the nature of the hydrogel adhesive, hydrogel adhesives can be used alone--without a conventional PSA to secure the electrode to the skin. This is a result of the hydrogel's own specific adhesive properties.

Hydrogel adhesives differ from conventional PSA's in several respects. PSA's generally consist of polyacrylate polymer, or a polyolefin polymer combined with a tackifier additive. Monomers used to prepare polyacrylate PSA's are
 25 long chain esters of acrylic acid such as octyl acrylate. These particular polymers are inherently tacky and adhesive in nature. Polyolefin-based PSA's are prepared from rubber-like polymers such as polybutylene. Because these polymers are not inherently tacky, a tackifier is blended into the polymer base. Terpenes are generally used as tackifiers in these compositions. Most significantly, a conventional PSA contains no solvent, is non-aqueous, and will not dry out. These polymers are inherently adhesive and do not depend upon a swollen, crosslinked, watery formulation to
 30 provide tackiness and peel adhesion. They cannot be made electrically conductive by addition of water and electrolyte and they tend to be less skin friendly than hydrogel adhesives. Examples of typical PSA's are the adhesives coated on "Scotch" brand cellophane tape, masking tape, medical adhesive tape, and "Band-Aid" brand adhesive bandages.

Hydrogel skin adhesives have proven useful in a variety of applications involving biomedical electrodes. Examples of such applications include use with electrocardiographic (ECG) electrodes, electrosurgical grounding pads, defibril-
 35 lation electrodes, transcutaneous nerve stimulation electrodes, and iontophoretic drug delivery electrodes. Non-electrode applications are also becoming increasingly important. Examples include use with transdermal drug delivery patches, as adhesives for ostomy devices, as wound dressings, and with medical tapes.

Hydrogel skin adhesive compositions are generally composed of a crosslinked water soluble polymer network swollen with water as a solvent component. Humectant materials are usually added as co-solvents to provide slow
 40 drying or non-drying characteristics to the hydrogel adhesive. Humectant materials are usually polyols such as glycerol, sorbitol, or propylene glycol, or low molecular weight polyethylene oxide diols such as PEG 400 or PEG 600. Other additives can also be added to hydrogel adhesives for specific purposes. Examples include electrolytes such as sodium chloride for electrical conductivity, preservatives such as methyl paraben to prevent microbiological degradation, buffering agents such as sodium dihydrogen phosphata for pH control, and water soluble polymers such as polyacrylamide
 45 for viscosity modification.

The crosslinked water soluble polymer network can be formed by polymerization of a large variety of water soluble monomers in the presence of difunctional crosslinking agents by free radical polymerization techniques initiated by thermal or photochemical methods. Crosslinking of previously formed water soluble polymers can also be effected by
 50 complexation with difunctional species, such as divalent metal cations or difunctional organic reactants, or by exposure to ionizing radiation such as gamma-rays or electron beams. Many naturally occurring polymers such as gelatin can be reversibly and non-covalently crosslinked by manipulating gelation temperatures.

Examples of water soluble monomers subject to free radical polymerization for use as a hydrogel are acrylic acid, methacrylic acid, acrylamide, methacrylamide, and vinyl pyrrolidone. Diacrylate esters of polyethylene oxides are typ-
 55 ical free radical crosslinking agents used in these compositions. Examples of hydrogel formation by the crosslinking of water soluble polymers are the crosslinking of carboxymethylcellulose by reaction with aluminum ion, the crosslinking of prepolymer polyisocyanates by reaction with water and organic diols, and the crosslinking of polyvinylpyrrolidone by electron beam radiation. Examples of naturally occurring polymers which form gels by thermal gelation are gelatin and karaya gum. There are thus a large number of hydrogel adhesives of diverse types.

One of the critical properties determining the usefulness of a hydrogel adhesive is its peel adhesion strength. High peel strength allows the hydrogel adhesive to be used without an accompanying PSA in many applications. Hydrogel skin adhesives with high peel strength provide a more secure attachment of electrodes (or other devices) to the patient. Correspondingly, low peel strength provides a less secure attachment, allowing easier removal of the hydrogel adhesive from the patient. Depending on the particular application, varying hydrogel adhesive peel strengths are required.

Another useful property of hydrogel adhesives is repositionability. "Repositionability" is defined as the ability of the adhesive hydrogel to be removed from one area of the skin and to be attached to another area without loss of peel adhesion properties. Other properties of hydrogel adhesives include tack adhesion and creep compliance.

The properties of the given hydrogel adhesive depend in large measure upon the nature of the cross-linked water soluble polymer that comprises the hydrogel adhesive. Presently, the nature of the cross-linked water soluble polymer used in the hydrogel adhesive fixes the properties of that adhesive. In order to vary the peel strength or repositionability of the adhesive, for example, different water soluble polymers may be used. Development of hydrogel adhesive properties is thus an empirical process at present. A water soluble polymer system that allows broad variation of hydrogel adhesive properties without changing the type of polymer is desirable.

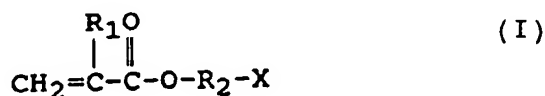
EP-A-0352442 is directed to pressure-sensitive adhesives for use in the paper industry. The adhesives are formed by using metal chelates to cross-link low molecular weight polymers of β -acryloyloxypropionic acid with gelatin. The pressure-sensitive adhesives produced according to this reference are water soluble or organic solvent soluble.

EP-A-0382128 is directed to a hydrogel to be coated onto a metal foil and used as a wound dressing. The hydrogel is formed by using metal chelates to cross-link polymers of at least one vinylcarboxylic acid and at least one of its alkali or ammonium salts. The hydrogel formed by cross-linking polymers as taught in this reference is not adhesive.

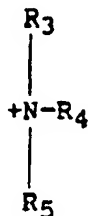
An article titled "The Effect of Acrylic Acid Dimer on the Properties of Carboxy Cement", appearing in J. Dent., Vol 16, 1988, pages 76-79, presents generally the impact of the addition of the acrylic acid dimer on the compressive and tensile strength of carboxy cements used in dental applications. Specifically, the reference discloses compositions formed by copolymerising β -acryloyloxypropionic acid polymer with acrylic acid polymer using zinc oxide or magnesium oxide to cross-link the polymers. The polymerisation is accomplished by a thermal or redox process. All the polymers used in forming this compound are short, linear, low molecular weight polymers. No hydrogel is formed according to this reference. This article concludes, as summarised in Table I of the reference, that the addition of β -acryloyloxypropionic acid decreases the strength of the resulting cement.

Summary of the Invention

The present invention provides a hydrogel adhesive made of a polymer formed by polymerising a monomer having the structure (I)



where R_1 is selected from H and CH_3 ; R_2 is selected from a straight or branched chain alkyl radical of 2-12 carbon atoms, a straight or branched chain aliphatic ester radical of 5-12 carbon and oxygen atoms, and a straight or branched chain ether radical of 3-12 carbon and oxygen atoms; X is an ionic group selected from SO_3^- , COO^- , and

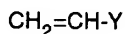


where R_3 , R_4 , and R_5 are independently selected from H and alkyl groups of 1-4 carbon atoms.

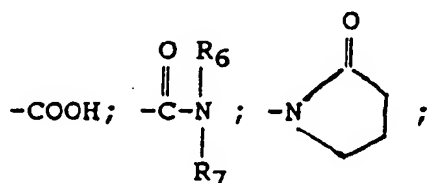
Also provided is a method of adhering a biomedical device to skin by disposing between the device and the skin the above hydrogel adhesive and applying sufficient pressure to the device to adhere it to the skin. A biomedical device with a surface adapted to be adhered to the skin of a patient, wherein the surface has the above hydrogel adhesive disposed thereon, is also provided by the present invention.

Also provided is a method of preparing the above hydrogel adhesive by polymerizing monomer (I) in the presence of multifunctional crosslinking agents by free radical polymerization techniques using an initiator.

The invention further provides compound that is a copolymer formed by copolymerizing a first water soluble monomer having the structure (I) with a second water soluble monomer having the structure (II)



where Y is selected from



$-\text{SO}_3\text{H}$; and $-\text{PO}_3\text{H}$ where R_6 and R_7 are independently selected from H and alkyl groups of 1-3 carbon atoms.

Also provided is a hydrogel adhesive comprising a copolymer formed by copolymerising the first and second water soluble monomers (I) and (II) above.

Also provided is a method of adhering a biomedical device to skin by disposing between the device and the skin a hydrogel adhesive made from monomers (I) and (II), as described above, and applying sufficient pressure to the device to adhere it to the skin.

Also provided is a biomedical device with a surface adapted to be adhered to the skin of a patient, wherein the surface has a hydrogel adhesive made from monomers (I) and (II) as described above.

Also provided is a method of preparing a hydrogel adhesive by copolymerising monomers (I) and (II) in the presence of multifunctional cross-linking agents by free radical polymerisation techniques using an initiator.

BRIEF DESCRIPTION OF THE DRAWING

The invention is best understood from the following detailed description when read in connection with the accompanying drawing, in which:

Fig. 1 is a graph depicting properties of a set of hydrogel adhesives prepared from exemplary formula (I) and formula (II) monomers;

Fig. 2 is a graph depicting properties of another set of hydrogel adhesives prepared from further exemplary formula (I) and formula (II) monomers;

Fig. 3 is a graph depicting properties of another set of hydrogel adhesives prepared from further exemplary formula (I) and formula (II) monomers;

Fig. 4 is a graph depicting properties of another set of hydrogel adhesives prepared from further exemplary formula (I) and formula (II) monomers;

Fig. 5 is a graph depicting properties of a set of hydrogel adhesives prepared from two exemplary formula (I) monomers; and

Fig. 6 is a cross-sectional view illustrating an exemplary biomedical electrode including a hydrogel adhesive of the present invention.

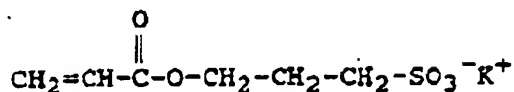
DETAILED DESCRIPTION OF THE INVENTION

The present invention involves hydrogel adhesives having variable properties depending on the relative proportions of the first and second water soluble monomers used in the formulation of the adhesive. The general formula for the first monomer is given above as formula I.

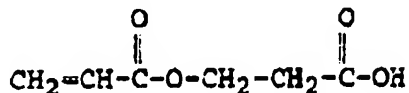
Two specific monomers within the scope of general formula I are potassium-3-sulfopropyl acrylate (SPAK) and

2-carboxyethylacrylate (CEA). CEA is particularly preferred when it is in the form of a partially neutralized alkali metal salt. The structures for these water soluble monomers are:

A. SPAK



B. CEA



The two formula I monomers given above are acrylate ester monomers. Other monomers having the general structure of formula I are methacrylate ester monomers such as 2-sulfoethylmethacrylate (SEMA), potassium-3-sulfo-propyl methacrylate (SPMAK), and methacryloxyethyl trimethylaminonium chloride (MAETAC).

The general formula for the second monomer used in the hydrogel adhesive compositions of the present invention is given above as formula II. The second monomer has a pendant chain smaller in molecular size than that of the first monomer. Examples of monomers of formula II are acrylic acid, acrylamide, alkylated acrylamides, vinyl pyrrolidone, vinyl sulphonic acid and vinyl phosphonic acid.

In one embodiment the present invention provides a hydrogel adhesive wherein said first water soluble monomer is 2-carboxy-ethylacrylate, said second water soluble monomer is acrylamide, and said first water soluble monomer comprises 10-50 weight % of total monomer weight.

A hydrogel adhesive formed by polymerising a formula I monomer without a formula II monomer (a homopolymer of the formula I monomer) will process certain adhesive properties. By adding increasing amounts of the formula II monomer and polymerising to form a copolymer of formula I and II monomers, the adhesive properties vary, depending on the relative proportions of the formula I and II monomers.

The preparation and composition of an adhesive hydrogel using a homopolymer of SPAK (100% of first water soluble polymer - SPAK; 0% of second water soluble polymer) is first described below. This serves as a general description of the procedure used to formulate the adhesive poly(meth)acrylate ester hydrogels of the invention. (The final composition of the hydrogel formed of the homopolymer of SPAK is given as Example 1 in Table 1; the compositions of all other examples disclosed herein are presented in the accompanying Tables 1-6 as Examples 2-34).

A mixture of potassium chloride (0.5g) and potassium-3-sulphopropylacrylate (35.0g) was dissolved in 40.5g of distilled water with stirring. Polyacrylamide N-300 LMW (2.0g) (available from American Cyanamid Co. of Wayne, New Jersey 07470) was then added and dispersed into the above solution with vigorous stirring. The polyacrylamide dissolved slowly over a period of a few hours with a corresponding increase in the viscosity of the solution. Glycerin (20.0g); a 3% solution of N,N'-methylenebis acrylamide in propylene glycol (1.2g); and Darocur 1173 (0.8g) (available from E M Industries Inc. of Hawthorne, New York 10532) were then added sequentially, with stirring, resulting in a moderately viscous, homogenous solution.

The finished composition was coated onto a polycarbonate film having a thickness of 2.5mm (mil), using a 30mm (mil) wet-film applicator. The coating was cured with a Fusion 78.74W/cm (200 W/in) UV lamp (H-bulb) at a bulb height of approximately 30.48cm (12 inches) with a UV dosage of 0.69 J/cm². A hydrogel adhesive was thus formed of a homopolymer of SPAK.

To measure peel adhesion, the coated hydrogel adhesive films were attached to a 3.2mm (1/8 inch) thick polyethylene foam substrate and pulled off at a 90° angle at a rate of 152.4mm (6 inches) per minute. The results were reported as grams per 22.2mm (7/8 inch) width of sample. Other properties measured were tack adhesion, creep compliance and repositionability. Tack adhesion was measured using a Polyken Tack instrument (2 sec. dwell, 1 cm/sec. speed, 20 grams force). Repositionability was measured by repeatedly pulling the adhesive off the foam substrate and measuring changes in peel adhesion.

In the description given above for the formation of an adhesive hydrogel, the distilled water serves as a solvent and potassium chloride is added as an electrolyte to provide electrical conductivity to the compositions of the invention when they are used as biomedical electrode adhesives. Potassium hydroxide is used to partially neutralise acrylate monomers containing carboxylic acid groups such as acrylic acid. Polyacrylamide polymer (PAAm N-300 LMW) serves

as a viscosity modifier. Glycerin serves as a humectant. Used as a cross-linking monomer for the hydrogel homopolymer is N,N'-methylenebis acrylamide (MBA) which, as described above, is added as a 3% solution in propylene glycol. (Although a difunctional cross-linking agent is used in this example, other multifunctional agents can be used. Thus, in this application, the term "multifunctional" includes difunctional, trifunctional, tetrafunctional, etc.) Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-propane-1-one) serves as the photoinitiator in the UV polymerization reaction.

The homopolymer of SPAK in the form of an adhesive hydrogel, synthesized as described in Example 1, exhibits a low peel strength (thereby minimizing risk of injury and discomfort to the patient) of 40 g as shown in Table 1, Example 1. The homopolymer also has good repositionability when attached to the skin. In terms of repositionability, the homopolymer of SPAK is superior to other hydrogel homopolymers such as polyacrylic acid.

Repositionability and low peel strength properties of hydrogel skin adhesives such as that formed of the SPAK homopolymer are important in biomedical applications such as diagnostic ECG electrodes, wound dressings, and medical tapes used to secure devices such as intravenous catheters to the body. Medical applications in the pediatric, neonatal, geriatric, and operating room areas are particularly relevant because of the high degree of skin sensitivity typically exhibited by patients within these hospital groupings.

To vary the properties of the hydrogel adhesive and provide greater peel strength, increased amounts (from 0% in the preceding example) of the second water soluble monomer are added and polymerized with the first monomer.

The preparation and composition of an adhesive hydrogel using a copolymer of SPAK and acrylic acid (AA) is next described. This serves as a description of the procedure used to formulate the adhesive copolymer poly(meth)acrylate ester hydrogels of the invention. The final composition of the hydrogel formed of the copolymer of this example is given as Example 4 in Table 1.

A mixture of potassium chloride (0.5 g) and potassium hydroxide (8.96 g) was dissolved in 34.54 g of distilled water with stirring while cooling to below 30 degrees C. Using an addition funnel, acrylic acid (19.38 g) was charged slowly and the temperature was maintained below 40 degrees C. After adding and dissolving potassium-3-sulfopropylacrylate (15.62 g), polyacrylamide N-300 LMW (2.0 g) was then added and dispersed into the above solution with vigorous stirring. The polyacrylamide dissolved slowly over a period of a few hours with a corresponding increase in the viscosity of the solution. Glycerin (17.0 g); a 3% solution of N,N'-methylenebis acrylamide in propylene glycol (1.2 g); and Darocur 1173 (0.8 g) were then added sequentially, with stirring, resulting in a moderately viscous, homogeneous solution.

In the description given above in Example 4 for the formation of an adhesive hydrogel, as in Example 1, the distilled water serves as a solvent and potassium chloride is added as an electrolyte to provide electrical conductivity. Potassium hydroxide, polyacrylamide polymer, glycerin, MBA, and Darocur 1173 serve the same functions as indicated in Example 1.

The finished composition was coated onto a polycarbonate film having a thickness of 2.5 mil, using a 30 mil wet-film applicator. The coating was cured as in Example 1. A hydrogel adhesive was thus formed of a copolymer of SPAK and acrylic acid. Peel adhesion, tack adhesion, creep compliance, and repositionability of the adhesive were then measured as in Example 1. The peel adhesion characteristics of a set of hydrogel adhesive copolymers prepared from acrylic acid as the second water soluble monomer and SPAK as the first are shown as Examples 1-7 in Table 1 and in Figure 1. The peel adhesion values exhibited by both of the homopolymers (40 g for the SPAK homopolymer and 30 g for the AA homopolymer) are low but adequate, for example, on applications on highly sensitive skin. The peel adhesion values of the copolymers are higher, however, than each of the homopolymers and increase to a peak level at a SPAK concentration of approximately 30-70 weight percent of the total monomer. The peak peel adhesion values for the copolymer are approximately 460 g, over ten times that of either of the homopolymers. The magnitude of the increased peel adhesion of copolymers having 25-75 weight % SPAK of total monomer (75-25 weight % AA of total monomer, respectively) over the homopolymers is unexpected. (See Figure 1.)

That the increase and peak in peel strength is unexpected is illustrated partly by the more linear variation in the tack adhesion of the same compositions as shown in Figure 1. Given this more linearized plot, linear variance of peel adhesion would also be expected. The variation in tack adhesion is almost linear and decreases as the concentration of SPAK in the copolymer increases.

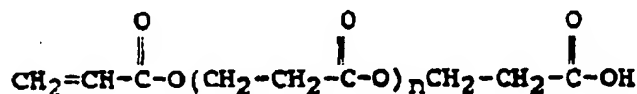
The SPAK/AA copolymer in hydrogel adhesive form is a particularly useful composition because it provides a continuum of hydrogel adhesives which can be used in a broad spectrum of applications. The applications can have requirements varying from a relatively weak, skin-friendly, repositionable adhesive (where a composition having a concentration close to either 100% SPAK or 0% SPAK would be appropriate) to an aggressive, very strong adhesive, desirable in such dynamic or long-term applications as ECG or Holter monitoring (where a 30-70% SPAK composition would be appropriate). Any intermediate adhesive characteristics which may be desired can also be produced. One should also appreciate that by varying the concentrations of the various components in the compositions, the peel adhesion peak can be shifted anywhere in the range of 10-90% by weight SPAK of total monomer.

Other monomers can also be used as the second water soluble monomer. Hydrogel adhesive copolymers prepared from acrylamide as the second monomer (AAM) and SPAK as the first possess synergistic adhesion properties analogous to those observed for SPAK/AA copolymers. (See the compositions and their corresponding adhesion data in

Examples 8-12 in Table 2 and Figure 2.) Similar to the other homopolymers described above, the peel adhesion exhibited by the AAM homopolymer (0% SPAK) is very low. Nevertheless, the peel adhesion of the copolymer increases and peaks at a SPAK concentration of approximately 20-70 weight percent of total monomer.

Although acrylic acid and acrylamide are the only specific examples of the second monomer given, alkylated acrylamides are reasonable extensions of acrylamide because they have similar polarity and size. vinyl pyrrolidone is also similar in size and polarity to dialkylated acrylamides. Sulfonic acid and phosphoric acid groups are reasonable extensions of the carboxylic acid group because they are also similar in size and polarity especially when neutralized to their anionic form. All of these monomers are within the scope of Formula II.

Turning to the second of the two formula I monomers which specifically illustrate the advantageous properties of the acrylate ester hydrogels of the present invention, CEA, it should be noted that the CEA which was used in the examples described herein is not a pure material. The CEA (or 2-carboxyethylacrylate) was obtained from Radcure Specialties Inc. of Louisville, Kentucky. It consists of a mixture of approximately 20% AA, 40% CEA, and 40% of a mixture of polyester trimers and tetramers having the following structure:



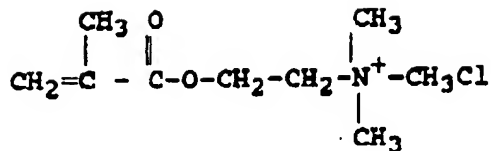
where $n = 0$ for CEA, $n = 1$ for trimer, and $n = 2$ for tetramer. Therefore, all of the hydrogel polymers and copolymers of CEA contain substantial quantities of polyester trimer and tetramer units and AA units as well as CEA. All numbers in the examples are corrected to account for the presence of these other substances.

CEA copolymers with AA or AAM (Examples 13-24, Tables 3 and 4, and Figures 3 and 4) exhibit adhesive behavior similar to that of the SPAK examples discussed above. The CEA as purchased (with 20% AA), which exhibits a 230 g peel adhesion, also possesses desirable repositionability properties. Copolymers of CEA with AA or AAM exhibit a surprising peel adhesion behavior within a useful range of peel adhesion values. In particular, peel adhesion values are surprisingly high when CEA is 20-75 weight % of the total monomer. The surprising peel adhesion behavior of CEA copolymers demonstrates that esters of longer chain length than SPAK or pure CEA also confer advantageous adhesion properties on the hydrogels of the present invention. Because the CEA used in the examples contains 40% of a mixture of trimer and tetramer which have 7 and 12 chain atoms, respectively, extrapolation to pure alkyl groups and ether groups is reasonable because these groups have similar hydrophobicity and polarity to the ester groupings present in CEA trimer and tetramer. Therefore, these groups are included in the general formula I for the first water soluble monomer.

Hydrogel-copolymer adhesives prepared from various ratios of SPAK and CEA together (i.e., two Formula I monomers) do not exhibit the surprising peel adhesion characteristics. Instead, a nearly linear relationship between the peel adhesion and the tack adhesion of the two homopolymers is observed (Examples 25-28, Table 5, and Figure 5). Because both SPAK and CEA are long-chain acrylate ester monomers, it is evident that only copolymers which combine long-chain acrylate ester monomers with monomers of small molecular size, such as AA or AAM, will exhibit the synergistic peel adhesion properties.

Hydrogel adhesive polymers were also prepared from methacrylate ester monomers as the Formula I monomers (Table 6) such as 2-sulfoethylmethacrylate (SEMA, Examples 29, 33, and 34) and potassium-3-sulfopropyl methacrylate (SPMAK, Examples 30 and 32). Methacrylate ester monomers are much less reactive to UV free radical initiation than are acrylate ester monomers such as SPAK and CEA; therefore, the formation of polymers comprising these compounds was initiated using thermal free radical initiator procedures. The thermal initiator used was V-50 (2,2'-azobis (2-amidinopropane) dihydrochloride) (available from Wako Chemicals, USA Inc. of Richmond, Virginia). The methacrylate monomers formed hydrogel adhesive polymers which were tacky and adhesive to the touch and may be as useful as the corresponding acrylate polymer hydrogels.

A cationic-terminated, methacrylate ester-based hydrogel adhesive was prepared by thermal initiation of the methacryloxyethyl trimethylammonium chloride monomer (MAETAC, Examples 31 and 34) having the following structure:



The resulting hydrogel polymer was also tacky and adhesive to the touch and appears to be as useful as all of the preceding examples.

A particularly useful application of the hydrogel adhesives of the present invention is with biomedical electrodes. The adhesives are useful in a wide variety of electrodes assuming varying construction. Figure 6 is an exemplary embodiment of one of these electrodes.

In Figure 6, a support member 1, which is circular in shape in this exemplary embodiment, is made of a plastic substance. Electrode 2 is incorporated in support member 1 so as to protrude from both sides of support member 1. An electrically conductive hydrogel adhesive 3, having a composition according to the present invention, is superposed on surface 4 of support member 1 and is adapted to be adhered to the skin of a patient. Hydrogel adhesive 3 should be applied to surface 4 in a thickness sufficient to cover the portion of electrode 2 protruding from surface 4 of support member 1.

In use, electrode 2 is connected to a measuring instrument (not shown) and the electrically conductive hydrogel adhesive 3 is pressed against the patient with sufficient pressure to adhere the biomedical electrode to the patient.

Table 1

Composition (% by weight)	Example Number						
	1	2	3	4	5	6	7
Distilled Water	40.05	29.77	32.86	34.54	36.36	37.95	39.05
Potassium Chloride	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Potassium Hydroxide	-	16.12	11.49	8.96	6.24	3.85	2.19
Acrylic Acid	-	35	24.95	19.38	13.4	8.29	4.7
SPAK	35	-	10.05	15.62	21.6	26.71	30.03
PAAM N-300 LMW	2	2	2	2	2	2	2
Glycerin	20	14.61	16.15	17	17.9	18.7	19.26
3MBBA/PO	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Darocur-1173	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Ave. Peel Force (g)	40	30	85	460	225	150	120
Tack Force (g)	63	408	375	310	233	175	144

Table 2

Composition (% by weight)	Example Number				
	8	9	10	11	12
Distilled Water	40.5	40.5	40.5	40.5	40.5
Potassium Chloride	0.5	0.5	0.5	0.5	0.5
Acrylamide	35	24.85	19.26	13.29	8.2
SPAK	-	10.15	15.74	21.72	26.8
PAAm N-300 LHM	2	2	2	2	2
Glycerin	20	20	20	20	20
3AMB/PG	1.2	1.2	1.2	1.2	1.2
Darocur-1173	0.8	0.8	0.8	0.8	0.8
Ave. Peel Force (g)	50	210	240	160	60
Tack Force (g)	420	330	315	250	93

Table 3

Composition (% by weight)	Example Number						
	13	14	15	16	17	18	19
Distilled Water	31.06	31.19	31.72	32.21	33.27	33.95	35.11
Potassium Chloride	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Potassium Hydroxide	14.44	13.36	12.82	12.03	10.69	9.62	7.93
AA (including the 20% AA in the CEA as purchased)	29.4	25.66	23.8	21	16.34	12.6	7.20 ^a
CEA (including the tri- and tetra-mers)	5.6	9.34	11.2	14	18.66	22.4	28
PAHs N-300 LMW	2	2	2	2	2	2	2
Glycerin	15	15.75	15.96	16.26	16.54	16.93	17.46
30MBA/PG	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Darocur-1173	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Ave. Peel Force (g)	70	160	540	390	290	280	230
Tack Force (g)	406	366	384	244	261	117	138

Table 4

Composition (% by weight)	Example Number			
	20	21	22	23
Distilled Water	39.21	38.49	37.6	36.72
Potassium Chloride	0.5	0.5	0.5	0.5
Potassium Hydroxide	1.62	2.7	4.04	5.37
Acrylamide	27.92	23.22	17.37	11.56
CEA (including tri- and tetra-mers)	5.66	9.42	14.1	18.75
AA (20% of CEA as purchased)	1.42	2.36	3.53	4.69
PAAm N-300 LMW	2	2	2	2
Glycerin	19.67	19.31	18.86	18.42
3MBA/PG	1.2	1.2	1.2	1.2
Darocur-1173	0.8	0.8	0.8	0.8
Ave. Peel Force (g)	200	350	190	190
Tack Force (g)	480	351	206	240

Table 5

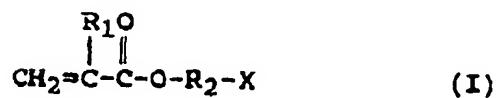
Composition (% by weight)	Example Number		
	25	26	27
Distilled Water	36	37.34	38.30
Potassium Chloride	0.5	0.5	0.5
Potassium Hydroxide	6.6	4.44	3.04
CBA (including tri- & tetra-mers)	23.30	15.50	10.72
AA (20% of CBA as purchased)	5.83	3.88	2.68
SPAK	5.87	15.62	21.6
PANAM N-300 LMW	2	2	2
Glycerin	17.9	18.72	19.08
3MBA/PG	1.2	1.2	1.2
Darocur-1173	0.8	0.8	0.8
Ave. Peel Force (g)	125	85	80
Tack Force (g)	80	104	68

Table 6

Composition (% by weight)	29	30	31	32	33	34
Distilled Water	38.7	42.7	47.67	39.87	37.51	39.9
Potassium Chloride	0.5	0.5	0.5	0.5	0.5	0.5
Potassium Hydroxide	5.95	-	-	3.59	6.84	3.25
Acrylic Acid	-	-	-	7.92	-	-
SEMA	35	-	-	-	20.09	14.34
CEA (including tri- & tetra- mers)	-	-	-	-	11.93	-
AA (20% of CEA as purchased)	-	-	-	-	2.98	-
SPMAK	-	35	-	27.08	-	-
HAETAC	-	-	35	-	-	20.66
Glycerin	18.45	20.4	15.43	19.04	17.95	19.15
3tMBA/PG	1.2	1.2	1.2	1.8	1.8	1.8
V-50	0.2	0.2	0.2	0.2	0.4	0.4

Claims

1. A hydrogel adhesive consisting essentially of a polymer formed by polymerizing a monomer having the structure (I)

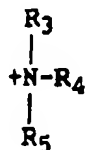


where,

R₁ is selected from the group consisting of H and CH₃;

R₂ is selected from the group consisting of a straight or branched chain alkyl radical of 2-12 carbon atoms, a straight or branched chain aliphatic ester of 5-12 carbon and oxygen atoms, and a straight or branched chain ether radical of 3-12 carbon and oxygen atoms;

X is an ionic group selected from the group consisting of SO₃⁻, COO⁻ and



where R₃, R₄, and R₅ are independently selected from the group consisting of H and alkyl groups of 1-4 carbon atoms.

2. A hydrogel adhesive as claimed in claim 1 wherein said monomer is selected from the group consisting of potassium-3-sulfopropyl acrylate, potassium-3-sulfopropyl methacrylate, 2-carboxyethylacrylate, 2-sulphoethylmethacrylate and methacryloxyethyl trimethyl-ammonium chloride.

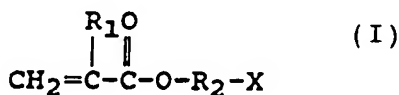
3. A method of adhering a biomedical device to skin comprising the steps of:

a. disposing between said device and the skin a hydrogel adhesive according to either one of Claims 1 and 2; and

b. applying pressure to said device to adhere said device to the skin.

4. A biomedical device comprising a surface adapted to be adhered to the skin of a patient, said surface having a hydrogel adhesive according to either one of Claims 1 and 2 thereon.

5. A method of preparing a hydrogel adhesive comprising polymerising a monomer having the structure (I)

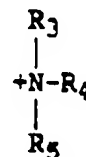


where,

R₁ is selected from the group consisting of H and CH₃;

R₂ is selected from the group consisting of a straight or branched chain alkyl radical of 2-12 carbon atoms, a straight or branched chain aliphatic ester of 5-12 carbon and oxygen atoms, and a straight or branched chain ether radical of 3-12 carbon and oxygen atoms;

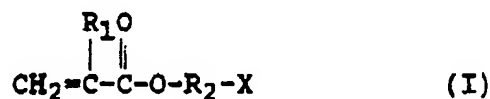
X is an ionic group selected from the group consisting of SO₃⁻, COO⁻ and



where R₃, R₄, and R₅ are independently selected from the group consisting of H and alkyl groups of 1-4 carbon atoms,

in the presence of a multifunctional crosslinking agent by a free radical polymerization technique.

6. A hydrogel adhesive comprising a copolymer formed by copolymerizing and cross-linking a first water soluble monomer having the structure (I)

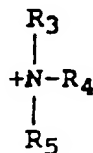


where,

R_1 is selected from the group consisting of H and CH_3 ;

R_2 is selected from the group consisting of a straight or branched chain alkyl radical of 2-12 carbon atoms, a straight or branched chain aliphatic ester of 5-12 carbon and oxygen atoms, and a straight or branched chain ether radical of 3-12 carbon and oxygen atoms;

X is an ionic group selected from the group consisting of SO_3^- , COO^- and

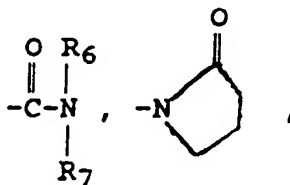


where R_3 , R_4 , and R_5 are independently selected from the group consisting of H and alkyl groups of 1-4 carbon atoms;

with a second water soluble monomer having the structure (II)



where Y is selected from the group consisting of $-\text{COOH}$,



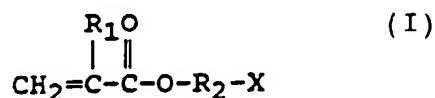
$-\text{SO}_3\text{H}$, and $-\text{PO}_3\text{H}$ where R_6 , R_7 are independently selected from the group consisting of H and alkyl groups of 1-3 carbon atoms;

in the presence of water, a multifunctional cross-linking agent, and a humectant.

7. A hydrogel adhesive as claimed in Claim 6 wherein said first water soluble monomer is selected from the group consisting of potassium-3-sulphopropyl acrylate, potassium-3-sulphopropyl methacrylate, 2-carboxyethylacrylate, 2-sulphoethylmethacrylate and methacryloxyethyl trimethylammonium chloride.
8. A hydrogel adhesive as claimed in either one of Claims 6 and 7 wherein said second water soluble monomer is selected from the group consisting of acrylic acid, acrylamide, alkylated acrylamides, vinyl pyrrolidone, vinyl sul-

phonic acid and vinyl phosphonic acid.

9. A hydrogel adhesive as claimed in any one of Claims 6 to 8 wherein said first water soluble monomer comprises 10-90 weight % of total monomer weight.
10. A hydrogel adhesive as claimed in Claim 6 wherein said first water soluble monomer is selected from the group consisting of potassium-3-sulphopropyl acrylate and potassium-3-sulphopropyl methacrylate, said second water soluble monomer is acrylic acid, and said first water soluble monomer comprises 10-90 weight % of total monomer weight.
11. A hydrogel adhesive as claimed in Claim 6 wherein said first water soluble monomer is selected from the group consisting of potassium-3-sulphopropyl acrylate and potassium-3-sulphopropyl methacrylate, and said second water soluble monomer is acrylamide, and said first water soluble monomer comprises 20-70 weight % of total monomer weight.
12. A hydrogel adhesive as claimed in Claim 6 wherein said first water soluble monomer is 2-carboxyethylacrylate, said second water soluble monomer is acrylic acid, and said first water soluble monomer comprises 20-75 weight % of total monomer weight.
13. A hydrogel adhesive as claimed in Claim 6 wherein said first water soluble monomer is 2-carboxyethylacrylate, said second water soluble monomer is acrylamide, and said first water soluble monomer comprises 10-50 weight % of total monomer weight.
14. A method of adhering a biomedical device to skin comprising the steps of:
 - a. disposing between said device and the skin a hydrogel adhesive according to any one of Claims 6 to 13; and
 - b. applying pressure to said device to adhere said device to the skin.
15. A biomedical device comprising a surface adapted to be adhered to the skin of a patient, said surface having a hydrogel adhesive according to any one of Claims 6 to 13 thereon.
16. A method of preparing a hydrogel adhesive comprising copolymerising a first water soluble monomer having the structure (I)

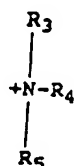


where,

R₁ is selected from the group consisting of H and CH₃;

R₂ is selected from the group consisting of a straight or branched chain alkyl radical of 2-12 carbon atoms, a straight or branched chain aliphatic ester of 5-12 carbon and oxygen atoms, and a straight or branched chain ether radical of 3-12 carbon and oxygen atoms;

X is an ionic group selected from the group consisting of SO₃⁻, COO⁻ and

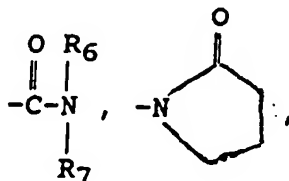


where R_3 , R_4 and R_5 are independently selected from the group consisting of H and alkyl groups of 1-4 carbon atoms,

with a second water soluble monomer having the structure (II)



where Y is selected from the group consisting of $-\text{COOH}$,



$-\text{SO}_3\text{H}$, and $-\text{PO}_3\text{H}$

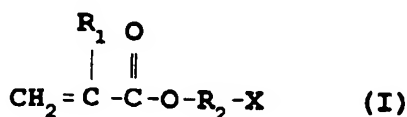
where R_6 , R_7 are independently selected from the group consisting of H and alkyl groups of 1-3 carbon atoms, in the presence of a multifunctional cross-linking agent by a free radical polymerisation technique.

17. The hydrogel adhesive as claimed in any one of Claims 7 to 14, further comprising an electrolyte, a neutralising agent, a viscosity modifier and a photoinitiator.

18. The hydrogel adhesive as claimed in claim 17, wherein said electrolyte is potassium chloride, said neutralizing agent is potassium hydroxide, said viscosity modifier is polyacrylamide polymer, said humectant is glycerin, said cross-linking agent is N,N'-methylenebis acrylamide in a 3% solution in propylene glycol, and said photoinitiator is 2-hydroxy-2-methyl-1-phenylpropane-1-one.

Patentansprüche

1. Ein Hydrogelklebstoff, der im wesentlichen aus einem Polymer besteht, das durch die Polymerisation eines Monomers mit der Strukturformel (I)

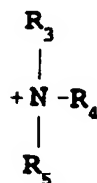


gebildet wird, wobei

R_1 aus der Gruppe bestehend aus H und CH_3 ausgewählt wird;

R_2 aus der Gruppe bestehend aus einem geradkettigen oder verzweigten Alkylradikal mit 2-12 Kohlenstoffatomen, einem geradkettigen oder verzweigten aliphatischen Ester mit 5-12 Kohlenstoff- und Sauerstoffatomen und einem geradkettigen oder verzweigten Etherradikal mit 3-12 Kohlenstoff- und Sauerstoffatomen ausgewählt wird;

X eine aus der Gruppe bestehend aus SO_3^- , COO^- und



ausgewählte Ionengruppe ist, wobei R_3 , R_4 und R_5 unabhängig voneinander aus der Gruppe bestehend aus H und Alkylgruppen mit 1-4 Kohlenstoffatomen ausgewählt werden.

2. Hydrogelklebstoff nach Anspruch 1, wobei das Monomer aus der Gruppe bestehend aus Kalium-3-sulfopropylacrylat, Kalium-3-sulfopropylmethacrylat, 2-Carboxyethylacrylat, 2-Sulfoethylmethacrylat und Methacryloxyethyltrimethylammoniumchlorid ausgewählt wird.

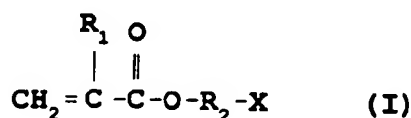
3. Ein Verfahren zur Anhaftung einer biologischmedizinischen Vorrichtung auf Haut, das aus den Schritten besteht:

a. zwischen der Vorrichtung und der Haut einen Hydrogelklebstoff gemäß einem der Ansprüche 1 und 2 zu plazieren; und

b. Druck auf die Vorrichtung auszuüben, um die Vorrichtung an die Haut zu kleben.

4. Eine biologisch-medizinische Vorrichtung, die eine Oberfläche umfaßt, die dazu ausgelegt ist, an die Haut eines Patienten gehaftet zu werden, wobei die Oberfläche mit einem Hydrogelklebstoff gemäß einem der Ansprüche 1 und 2 bestrichen ist.

5. Ein Verfahren zur Herstellung eines Hydrogelklebstoffs, das beinhaltet, ein Monomer mit der Strukturformel (I)

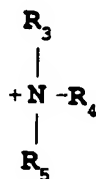


zu polymerisieren, wobei

R_1 aus der Gruppe bestehend aus H und CH_3 ausgewählt wird;

R_2 aus der Gruppe bestehend aus einem geradkettigen oder verzweigten Alkylradikal mit 2-12 Kohlenstoffatomen, einem geradkettigen oder verzweigten aliphatischen Ester mit 5-12 Kohlenstoff- und Sauerstoffatomen und einem geradkettigen oder verzweigten Etherradikal mit 3-12 Kohlenstoff- und Sauerstoffatomen ausgewählt wird;

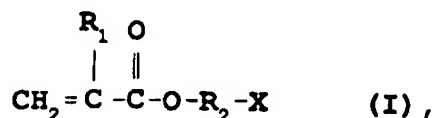
X eine aus der Gruppe bestehend aus SO_3^- , COO^- und



ausgewählte Ionengruppe ist, wobei R_3 , R_4 und R_5 unabhängig voneinander aus der Gruppe bestehend aus H und Alkylgruppen mit 1-4 Kohlenstoffatomen ausgewählt werden,

und zwar durch ein radikalisches Polymerisationsverfahren in Anwesenheit eines multifunktionellen Vernetzungsmittels.

6. Hydrogelklebstoff, der aus einem Copolymer besteht, der durch die Copolymerisation und Quervernetzung eines ersten wasserlöslichen Monomers mit der Strukturformel (I)

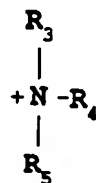


wobei

R₁ aus der Gruppe bestehend aus H und CH₃ ausgewählt wird;

R₂ aus der Gruppe bestehend aus einem geradkettigen oder verzweigten Alkylradikal mit 2-12 Kohlenstoffatomen, einem geradkettigen oder verzweigten aliphatischen Ester mit 5-12 Kohlenstoff- und Sauerstoffatomen und einem geradkettigen oder verzweigten Etherradikal mit 3-12 Kohlenstoff- und Sauerstoffatomen ausgewählt wird;

X eine aus der Gruppe bestehend aus SO_3^- , COO^- und

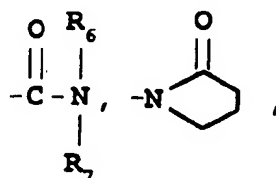


ausgewählte Ionengruppe ist, wobei R_3 , R_4 und R_5 unabhängig voneinander aus der Gruppe bestehend aus H und Alkylgruppen mit 1-4 Kohlenstoffatomen ausgewählt werden;

mit einem zweiten wasserlöslichen Monomer mit der Strukturformel (II)



gebildet wird, wobei Y aus der Gruppe bestehend aus -COOH,

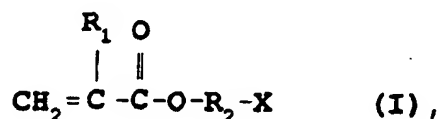


-SO₃H und -PO₃H ausgewählt wird, wobei R₆, R₇ unabhängig voneinander aus der Gruppe bestehend aus H und Alkylgruppen mit 1-3 Kohlenstoffatomen ausgewählt werden;
und zwar in Anwesenheit von Wasser, eines multifunktionellen Vernetzungsmittels und eines Feuchthaltemittels.

7. Hydrogelklebstoff nach Anspruch 6, wobei das erste wasserlösliche Monomer aus der Gruppe bestehend aus Kalium-3-sulfopropylacrylat, Kalium-3-sulfopropylmethacrylat, 2-Carboxyethylacrylat, 2-Sulfoethylmethacrylat

und Methacryloxyethyltrimethylammoniumchlorid ausgewählt wird.

8. Hydrogelklebstoff nach einem der Ansprüche 6 und 7, wobei das zweite wasserlösliche Monomer aus der Gruppe bestehend aus Acrylsäure, Acrylamid, alkylierten Acrylamiden, Vinylpyrrolidon, Vinylsulfonsäure und Vinylphosphonsäure ausgewählt wird.
9. Hydrogelklebstoff nach einem der Ansprüche 6 bis 8, wobei das erste wasserlösliche Monomer 10-90 Gew.-% des Monomergesamtgewichts umfaßt.
10. Hydrogelklebstoff nach Anspruch 6, wobei das erste wasserlösliche Monomer aus der Gruppe bestehend aus Kalium-3-sulfopropylacrylat und Kalium-3-sulfopropylmethacrylat ausgewählt wird, das zweite wasserlösliche Monomer Acrylsäure ist und das erste wasserlösliche Monomer 10-90 Gew.-% des Monomergesamtgewichts umfaßt.
11. Hydrogelklebstoff nach Anspruch 6, wobei das erste wasserlösliche Monomer aus der Gruppe bestehend aus Kalium-3-sulfopropylacrylat und Kalium-3-sulfopropylmethacrylat ausgewählt wird und der zweite wasserlösliche Monomer Acrylamid ist und der erste wasserlösliche Monomer 20-70 Gew.-% des Monomergesamtgewichts umfaßt.
12. Hydrogelklebstoff nach Anspruch 6, wobei das erste wasserlösliche Monomer 2-Carboxyethylacrylat ist, das zweite wasserlösliche Monomer Acrylsäure ist und das erste wasserlösliche Monomer 20-75 Gew.-% des Monomergesamtgewichts umfaßt.
13. Hydrogelklebstoff nach Anspruch 6, wobei das erste wasserlösliche Monomer 2-Carboxyethylacrylat ist, das zweite wasserlösliche Monomer Acrylamid ist und das erste wasserlösliche Monomer 10-50 Gew.-% des Monomergesamtgewichts umfaßt.
14. Verfahren zur Anhaftung einer biologischmedizinischen Vorrichtung auf Haut, das aus den Schritten besteht:
 - a. zwischen der Vorrichtung und der Haut einen Hydrogelklebstoff gemäß einem der Ansprüche 6 bis 13 zu platzieren; und
 - b. Druck auf die Vorrichtung auszuüben, um die Vorrichtung an die Haut zu kleben.
15. Eine biologisch-medizinische Vorrichtung, die eine Oberfläche umfaßt, die dazu ausgelegt ist, an die Haut eines Patienten angeklebt zu werden, wobei die Oberfläche mit einem Hydrogelklebstoff gemäß einem der Ansprüche 6 und 13 bestrichen ist.
16. Ein Verfahren zur Herstellung eines Hydrogelklebstoffs, das daraus besteht, ein erstes wasserlösliches Monomer mit der Strukturformel (I)

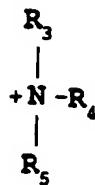


wobei

R₁ aus der Gruppe bestehend aus H und CH₃ ausgewählt wird;

R₂ aus der Gruppe bestehend aus einem geradkettigen oder verzweigten Alkylradikal mit 2-12 Kohlenstoffatomen, einem geradkettigen oder verzweigten aliphatischen Ester mit 5-12 Kohlenstoff- und Sauerstoffatomen und einem geradkettigen oder verzweigten Etherradikal mit 3-12 Kohlenstoff- und Sauerstoffatomen ausgewählt wird;

X eine aus der Gruppe bestehend aus SO₃⁻, COO⁻ und

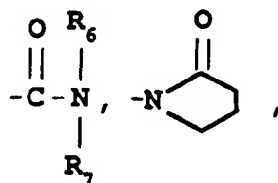


ausgewählte Ionengruppe ist, wobei R_3 , R_4 und R_5 unabhängig voneinander aus der Gruppe bestehend aus H und Alkylgruppen mit 1-4 Kohlenstoffatomen ausgewählt werden,

mit einem zweiten wasserlöslichen Monomer mit der Strukturformel (II)



zu copolymerisieren, wobei Y aus der Gruppe bestehend aus $-COOH$,



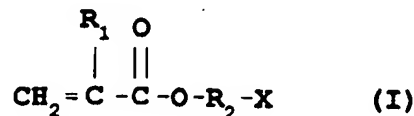
$-SO_3H$ und $-PO_3H$ ausgewählt wird, wobei R_6 , R_7 unabhängig voneinander aus der Gruppe bestehend aus H und Alkylgruppen mit 1-3 Kohlenstoffatomen ausgewählt werden, und zwar durch ein radikalisches Kettenpolymerisationsverfahren in der Anwesenheit eines multifunktionellen Vernetzungsmittels.

17. Der Hydrogelklebstoff gemäß einem der Ansprüche 7 bis 14, der weiterhin einen Elektrolyten, ein Neutralisationsmittel, einen Viskositätsveränderer und einen Fotoinitiator beinhaltet.

18. Hydrogelklebstoff gemäß Anspruch 17, wobei der Elektrolyt Kaliumchlorid, das Neutralisationsmittel Kaliumhydroxid, der Viskositätsveränderer ein Polyacrylamidpolymer, das Feuchthaltemittel Glycerin, das Vernetzungsmittel N,N'-Methylenbisacrylamid in einer 3%igen Lösung in Propylenglycol und der Fotoinitiator 2-Hydroxy-2-methyl-1-phenylpropan-1-on ist.

Revendications

1. Un adhésif hydrogel consistant essentiellement en un polymère formé en polymérisant un monomère ayant la structure (I)

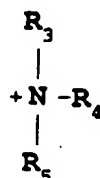


où,

R_1 est sélectionné à partir du groupe constitué de H et de CH_3 ;

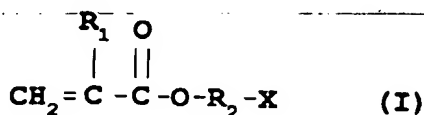
R₂ est sélectionné à partir du groupe constitué d'un radical alkyle en chaîne ramifiée ou droite d'atomes de carbone 2-12, d'un ester aliphatique en chaîne ramifiée ou droite d'atomes de carbone 5-12 et d'oxygène, et d'un radical d'éther en chaîne ramifiée ou droite d'atomes de carbone 3-12 et d'oxygène;

X est un groupe ionique sélectionné à partir du groupe constitué de SO₃⁻, de COO⁻ et de



où R₃, R₄ et R₅ sont indépendamment sélectionnés à partir du groupe constitué de H et de groupes alkyles d'atomes de carbone 1-4.

2. Un adhésif hydrogel selon la revendication 1 dans lequel ledit monomère est sélectionné à partir du groupe constitué d'acrylate de potassium-3-sulfopropyle, de méthacrylate de potassium-3-sulfopropyle, de 2-carboxyéthylacrylate, de 2-sulfoéthylméthacrylate et de chlorure d'ammonium triméthyle méthacryloxyéthyl.
3. Un procédé pour faire adhérer un dispositif biomédical à la peau comprenant les étapes consistant à:
 - a. disposer entre ledit dispositif et la peau un adhésif hydrogel selon l'une quelconque des revendications 1 et 2; et
 - b. appliquer une pression sur ledit dispositif pour faire adhérer ledit dispositif à la peau.
4. Un dispositif biomédical comprenant une surface adaptée pour adhérer à la peau d'un patient, ladite surface étant recouverte d'un adhésif hydrogel selon l'une quelconque des revendications 1 et 2.
5. Un procédé pour préparer un adhésif hydrogel comprenant la polymérisation d'un monomère ayant la structure (I)

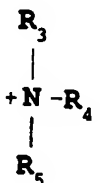


où,

R₁ est sélectionné à partir du groupe constitué de H et de CH₃;

R₂ est sélectionné à partir du groupe constitué d'un radical alkyle en chaîne ramifiée ou droite d'atomes de carbone 2-12, d'un ester aliphatique en chaîne ramifiée ou droite d'atomes de carbone 5-12 et d'oxygène, et d'un radical d'éther en chaîne ramifiée ou droite d'atomes de carbone 3-12 et d'oxygène;

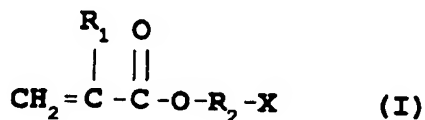
X est un groupe ionique sélectionné à partir du groupe constitué de SO₃⁻, de COO⁻ et de



où R_3 , R_4 et R_5 sont indépendamment sélectionnés à partir du groupe constitué de H et de groupes alkyles d'atomes de carbone 1-4,

en présence d'un agent de réticulation multifonctionnel par une technique de polymérisation de radical libre.

6. Un adhésif hydrogel comprenant un copolymère formé en copolymérisant et en réticulant un premier monomère soluble dans l'eau ayant la structure (I)

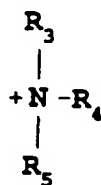


où,

R_1 est sélectionné à partir du groupe constitué de H et de CH_3 ;

R_2 est sélectionné à partir du groupe constitué d'un radical alkyle en chaîne ramifiée ou droite d'atomes de carbone 2-12, d'un ester aliphatique en chaîne ramifiée ou droite d'atomes de carbone 5-12 et d'oxygène, et d'un radical d'éther en chaîne ramifiée ou droite d'atomes de carbone 3-12 et d'oxygène;

X est un groupe ionique sélectionné à partir du groupe constitué de SO_3^- , de COO^- et de

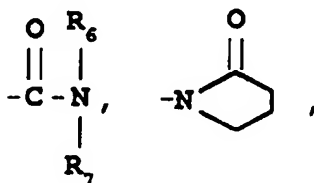


où R_3 , R_4 et R_5 sont indépendamment sélectionnés à partir du groupe constitué de H et de groupes alkyles d'atomes de carbone 1-4;

avec un second monomère soluble dans l'eau ayant la structure (II)



où Y est sélectionné à partir du groupe constitué de $-\text{COOH}$,



$-\text{SO}_3\text{H}$, et $-\text{PO}_3\text{H}$ où R_6 , R_7 sont indépendamment sélectionnés à partir du groupe constitué de H et de groupes alkyles d'atomes de carbone 1-3;

en présence d'eau, d'un agent de réticulation multifonctionnel, et d'un humectant.

7. Un adhésif hydrogel selon la revendication 6 dans lequel ledit premier monomère soluble dans l'eau est sélectionné à partir du groupe constitué d'acrylate de potassium-3-sulfopropyle, de méthacrylate de potassium-3-sulfopropyle, de 2-carboxyéthylacrylate, de 2-sulfoéthylméthacrylate et de chlorure d'ammonium triméthyle méthacryloxyéthyl.

8. Un adhésif hydrogel selon l'une quelconque des revendications 6 et 7 dans lequel ledit second monomère soluble dans l'eau est sélectionné à partir du groupe constitué de l'acide acrylique, de l'acrylamide, des acrylamides alkylés, du pyrrolidone vinyle, de l'acide sulfonique de vinyle et de l'acide phosphonique de vinyle.

9. Un adhésif hydrogel selon l'une quelconque des revendications 6 à 8 dans lequel ledit premier monomère soluble dans l'eau représente de 10 à 90 % en poids du poids total du monomère.

10. Un adhésif hydrogel selon la revendication 6 dans lequel ledit premier monomère soluble dans l'eau est sélectionné à partir du groupe constitué d'acrylate de potassium-3-sulfopropyle et de méthacrylate de potassium-3-sulfopropyle, ledit second monomère soluble dans l'eau est de l'acide acrylique, et ledit premier monomère soluble dans l'eau représente de 10 à 90 % en poids du poids total du monomère.

11. Un adhésif hydrogel selon la revendication 6 dans lequel ledit premier monomère soluble dans l'eau est sélectionné à partir du groupe constitué d'acrylate de potassium-3-sulfopropyle et de méthacrylate de potassium-3-sulfopropyle, et ledit second monomère soluble dans l'eau est de l'acrylamide, et ledit premier monomère soluble dans l'eau représente de 20 à 70 % en poids du poids total du monomère.

12. Un adhésif hydrogel selon la revendication 6 dans lequel ledit premier monomère soluble dans l'eau est du 2-carboxy-éthylacrylate, ledit second monomère soluble dans l'eau est de l'acide acrylique, et ledit premier monomère soluble dans l'eau représente de 20 à 75 % en poids du poids total du monomère.

13. Un adhésif hydrogel selon la revendication 6 dans lequel ledit premier monomère soluble dans l'eau est du 2-carboxy-éthylacrylate, ledit second monomère soluble dans l'eau est de l'acrylamide, et ledit premier monomère soluble dans l'eau représente de 10 à 50 % en poids du poids total du monomère.

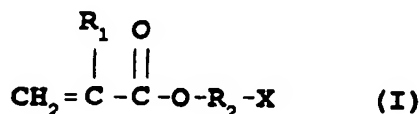
14. Un procédé pour faire adhérer un dispositif biomédical à la peau comprenant les étapes consistant à:

a. disposer entre ledit dispositif et la peau un adhésif hydrogel selon l'une quelconque des revendications 6 à 13; et

b. appliquer une pression sur ledit dispositif pour faire adhérer ledit dispositif à la peau.

15. Un dispositif biomédical comprenant une surface adaptée pour adhérer à la peau d'un patient, ladite surface étant recouverte d'un adhésif hydrogel selon l'une quelconque des revendications 6 à 13.

16. Un procédé pour préparer un adhésif hydrogel comprenant la copolymérisation d'un premier monomère soluble dans l'eau ayant la structure (I)

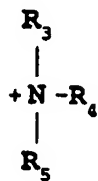


où,

R₁ est sélectionné à partir du groupe constitué de H et de CH₃;

R₂ est sélectionné à partir du groupe constitué d'un radical alkyle en chaîne ramifiée ou droite d'atomes de carbone 2-12, d'un ester aliphatique en chaîne ramifiée ou droite d'atomes de carbone 5-12 et d'oxygène, et d'un radical d'éther en chaîne ramifiée ou droite d'atomes de carbone 3-12 et d'oxygène;

X est un groupe ionique sélectionné à partir du groupe constitué de SO₃⁻, COO⁻ et

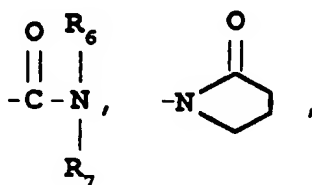


où R_3 , R_4 et R_5 sont indépendamment sélectionnés à partir du groupe constitué de H et de groupes alkyles d'atomes de carbone 1-4,

avec un second monomère soluble dans l'eau ayant la structure (II)



où Y est sélectionné à partir du groupe constitué de $-COOH$,



$-SO_3H$, et $-PO_3H$ où R_6 , R_7 sont indépendamment sélectionnés à partir du groupe constitué de H et de groupes alkyles d'atomes de carbone 1-3, en présence d'un agent de réticulation multifonctionnel par une technique de polymérisation de radical libre.

17. L'adhésif hydrogel selon l'une quelconque des revendications 7 à 14, comprenant en outre un électrolyte, un agent neutralisant, un modificateur de viscosité et un photoamorceur.

18. L'adhésif hydrogel selon la revendication 17, dans lequel ledit électrolyte est du chlorure de potassium, ledit agent neutralisant est de l'hydroxyde de potassium, ledit modificateur de viscosité est un polymère polyacrylamide, ledit humectant est de la glycérine, ledit agent de réticulation est du N,N'-méthylènebis acrylamide dans une solution de propylène glycol à 3 %, et ledit photoamorceur est du 2-hydroxy-2-méthyl-1-phényl-propane-1-one.

FIG. 1

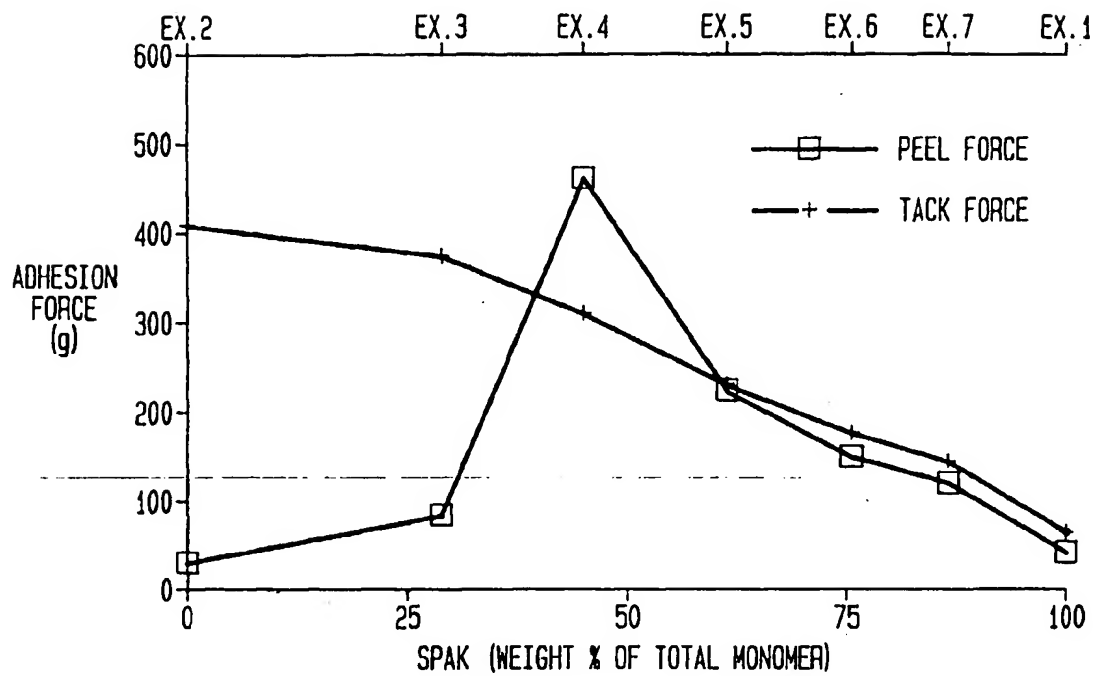


FIG. 2

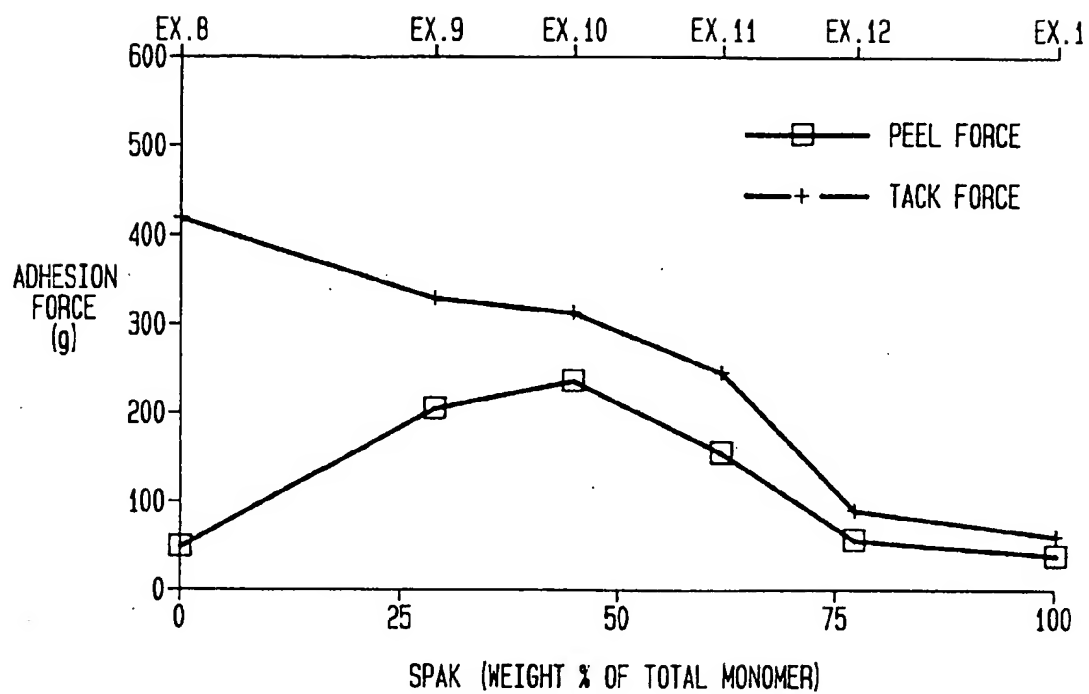


FIG. 3

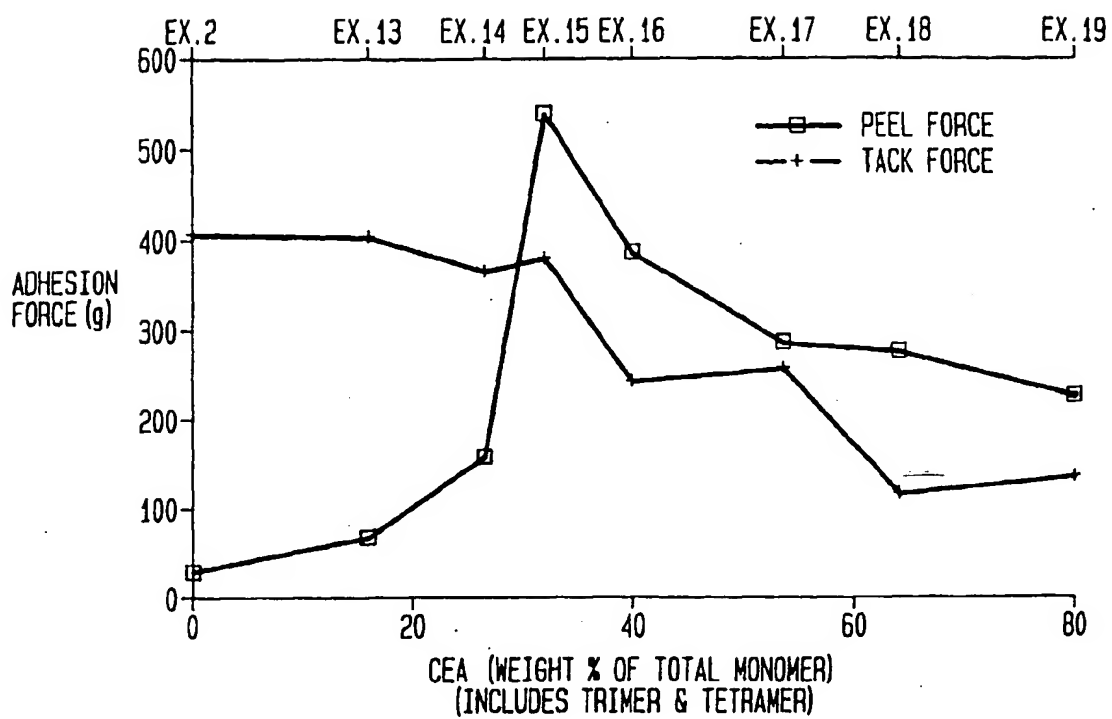


FIG. 4

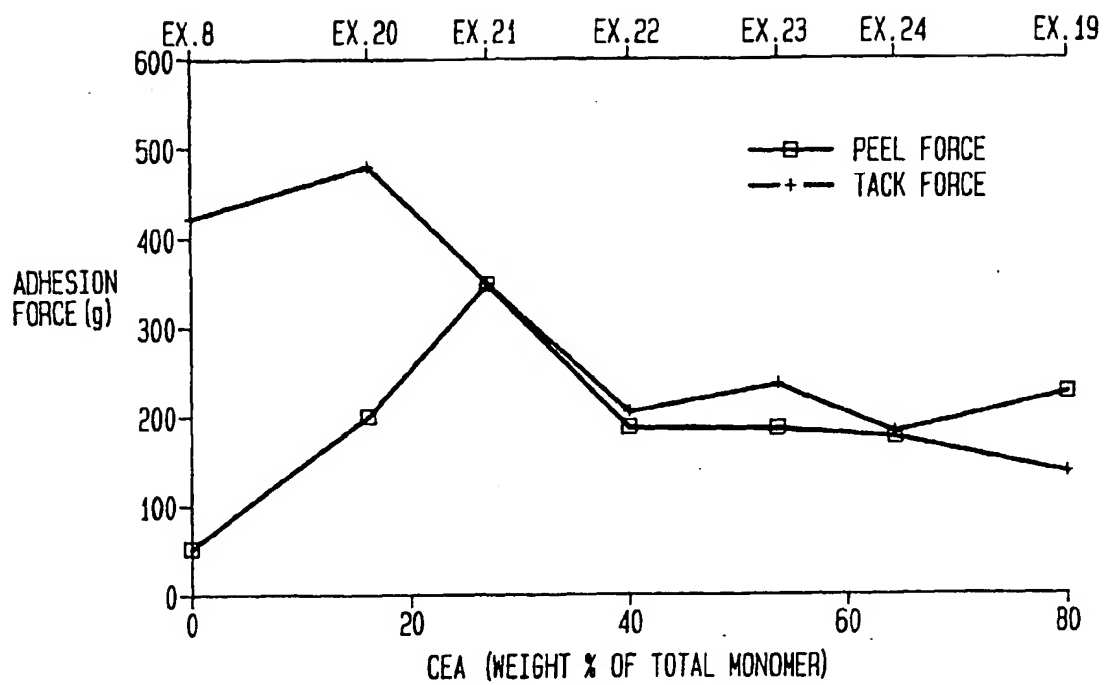


FIG. 5

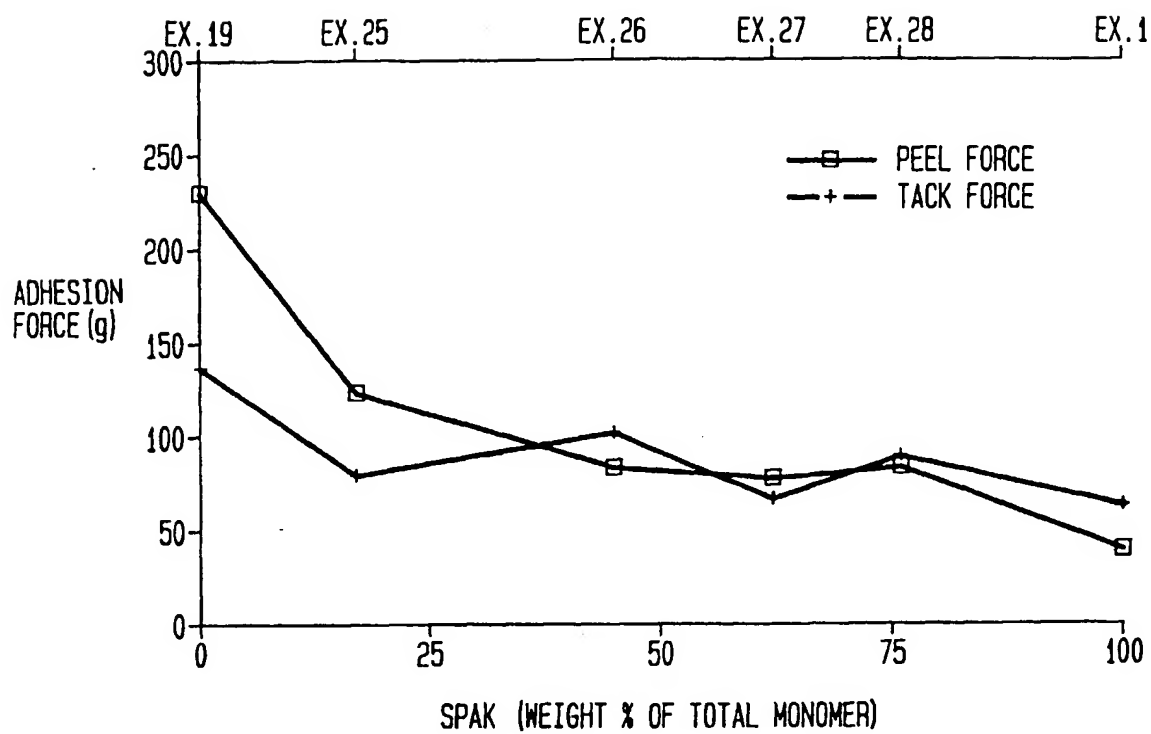


FIG. 6

